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USE OF COPOLYMERS DERIVED FROM POLYAMIDES AS GELLING AGENTS FOR RELATIVELY NONPOLAR COMPOUNDS

The present invention relates to the use of copolymers comprising at least polyoxyalkylenated polyamide functions, as gelling agents for relatively nonpolar compounds or for surfactants, which are preferably nonionic.

Although there are many possibilities for preparing aqueous gels, gels made of relatively nonpolar compounds or of surfactants have not been particularly developed, although many fields may be interested by the production of such gels. This is the case especially for the cosmetics field (for example suncreams); the field of industrial cleaning/stripping (treatment of vertical surfaces); the field of plant protection (maintenance in suspension of hydrolysis-sensitive active materials, for example); the field of printing inks; the field of detergency; the field of public works and construction; the papermaking field (for example the formulation of antifoams for manufacturing paper pulp); the explosives field (for example the gelation of ergols or propergols for military and civil applications) or the field of hydraulic fluids.

The aim of the present invention is to propose a simple and efficient means for gelling relatively nonpolar media or surfactant media.

Thus, one subject of the invention is the use as a gelling agent, of a relatively nonpolar compound or a nonionic surfactant, of at least one block copolymer comprising the following units:

$-X-(R^1)_m-(OA)_n-X-$ (I), and

$-[NH-R^2-NHCO-R'^2-CO]_r-$ (IIa), and/or

$-[NH-R^3-CO]_s-$ (IIb), and

$-OC-R^4-CO-$ (III)

in which units:

- X corresponds to the end function of said unit after reaction with an amine or carboxylic acid function;
- R^1, which may be identical or different, represent a linear or branched alkyl radical comprising 2 to 4 carbon atoms;
- OA, which may be identical or different, represent an oxyethylenated, oxypropylenated or oxybutylenated radical, or mixtures thereof;
- R^2, R'^2, R^3 and R^4, which may be identical or different, represent:
  - a linear or branched alkyl radical comprising 2 to 18 carbon atoms,
  - an aryl radical comprising one or more optionally substituted aromatic nuclei,
- m is equal to 0 or 1,
- n is an integer between 4 and 800,
- r is such that the number of amide bonds is between 1 and 15 per unit (I),
- s is such that the number of amide bonds is between 1

and 15 per unit (I),

- the molar ratio of the number of units (III) to the number of units (I) is between 0.5/1 and 1.4/1;
- the various units are linked together at least by means of amide bonds;
- the number-average molar mass of the copolymer is less than 100 000 g/mol.

However, other characteristics will emerge more clearly on reading the description and the examples which follow.

Before describing the copolymer used in the invention in more precise detail, the nature of the compound which may be gelled according to the invention will be given.

Thus, the expression "relatively nonpolar compound" means any constituent which is liquid at the temperature for preparing and/or using the formulation of which it forms one of the constituent elements.

Moreover, this liquid, which is in the Hansen solubility space (Handbook of solubility parameters and other cohesion parameters - Allan F.M. Barton, CRC Press Inc., 1983-), more particularly has the following parameters:

. δP of Keesom interactions of less than or equal to 16.5 $(J/cm^3)^{1/2}$

. δH of hydrogen bonds of less than or equal to 10.5 $(J/cm^3)^{1/2}$

. δD of London interactions of greater than or equal to

15 $(J/cm^3)^{1/2}$.

More particularly, the coefficient δP is between 2 and 16.5 $(J/cm^3)^{1/2}$.

Preferably, the coefficient δP is between 2 and 10.5 $(J/cm^3)^{1/2}$.

It should be noted that the coefficient δD is usually between 15 and 23.

As non-limiting examples of relatively nonpolar compounds, mention may be made of:

. triglycerides of saturated or unsaturated fatty acids containing at least 12 carbon atoms and preferably from 14 to 20 carbon atoms; these may be synthetic or, preferably, natural triglycerides, for instance plant oils such as rape seed oil, soybean oil, groundnut oil, butter oil, cottonseed oil, flax oil, coconut oil, olive oil, palm oil, grapeseed oil, fish oil, castor oil or copra oil;

. methyl esters of saturated or unsaturated fatty acids containing at least 12 carbon atoms and preferably from 14 to 20 carbon atoms, for instance methyl oleate;

. aliphatic or cyclic C_1-C_8 alkyl esters of saturated monocarboxylic acids, for instance methyl acetate, ethyl acetate or cyclohexyl acetate;

. terpenic compounds (D-limonene, L-limonene, etc.);

. C_1-C_4 alkyl diesters of at least one C_4-C_6 aliphatic diacid. Mixtures of diacid esters which are esters derived essentially from adipic acid, glutaric acid

and succinic acid are more particularly used, the alkyl groups of the ester portion being chosen especially from methyl and ethyl groups, but may also be propyl, isopropyl, butyl, n-butyl and isobutyl;

. anisole;

. n-methylpyrrolidone;

. dimethyl sulfoxide;

. ketones, for instance cyclopentanone or methyl isobutyl ketone;

. polyalkylene glycols, for instance polyethylene glcyol 400 or polypropylene glycol 400.

The present invention may be used for gelling a relatively nonpolar compound or a mixture of several such compounds.

Surfactants, and more particularly nonionic surfactants, may similarly be gelled according to the process of the present invention.

More particularly, the surfactant is in the form of a liquid at the temperature for preparing and/or using the formulation of which it forms one of the constituent elements.

In addition, the surfactant is preferably free of polar solvents, but, if such a solvent is present, the solvent content in this surfactant remains such that it does not prevent the subsequent gelation of said surfactant.

By way of nonionic surfactant which is most particularly suitable for the invention, mention may be

made, without, however, intending to be limited thereto, of:

. polyoxyalkylenated (polyethoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkylphenols in which the alkyl substituent is C_6-C_{12} and containing from 5 to 25 oxyalkylene units; examples which may be mentioned are Triton X-45, X-114, X-100 or X-102 sold by Rohm & Haas Co. and Igepal NP2 to NP17 from Rhodia Chimie;

. polyoxyalkylenated C_8-C_{22} aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units; examples which may be mentioned are the products Tergitol 15-S-9 and 24-L-6 NMW sold by Union Carbide Corp., Neodol 45-9, 23-65, 45-7 and 45-4 sold by Shell Chemical Co., Kyrol EOB sold by Procter & Gamble Co., Synperonic A3 to A9 from ICI and Rhodasurf IT, DB and B from Rhodia Chimie;

. products resulting from the condensation of ethylene oxide and/or propylene oxide with propylene glycol or ethylene glycol, with a weight-average molecular mass of about from 2 000 to 10 000, such as the Pluronic products sold by BASF;

. alkoxylated amido amines containing from 1 to 50, preferably from 1 to 25 and most particularly from 2 to 20 oxyalkylene (preferably oxyethylene) units;

. alkoxylated terpenic hydrocarbons such as ethoxylated and/or propoxylated α- or β-pinenes, containing from 1 to 30 oxyethylene and/or oxypropylene units; in

particular such as those described in international application WO 96/01245, to which reference may be made in particular;

. alkylpolyglycosides which may be obtained by condensation (for example by acid catalysis) of glucose with primary fatty alcohols (US-A-3 598 865; US 4 565 647; EP 132 043; EP 132 046, etc.) containing a C_4-C_{20} and preferably C_8-C_{18} alkyl group and also an average number of glucose units of about from 0.5 to 3 and preferably of about from 1.1 to 1.8 per mole of alkylpolyglycoside (APG); mention may be made in particular of those containing a C_8-C_{14} alkyl group and on average 1.4 glucose units per mole; a C_{12}-C_{14} alkyl group and on average 1.4 glucose units per mole; a C_8-C_{14} alkyl group and on average 1.5 glucose units per mole; a C_8-C_{10} alkyl group and on average 1.6 glucose units per mole; which are sold, respectively, under the names Glucopon 600 EC®, 600 CSUP®, 650 EC® and 225 CSUP® by Henkel.

The present invention makes it possible to gel one of the surfactants mentioned above, and also mixtures thereof.

The copolymer will now be described.

As mentioned above, the copolymer comprises units (I) to (III), which are more particularly randomly distributed.

The copolymer comprises amide bonds, ether bonds arising from the unit (I) and, depending on the

nature of the reactive functions of the unit (I), possibly ester and urethane bonds.

Moreover, the end functions of this copolymer are amines, more particularly primary amines, carboxylic acids and optionally alcohols.

The copolymer comprises at least one unit (I) of the following formula:

$$-X-(R^1)_m-(OA)_n-X-$$

in which formula:

- X corresponds to the end function of said unit after reaction with an amine or carboxylic acid function;
- R^1, which may be identical or different, represent a linear or branched alkyl radical comprising 2 to 4 carbon atoms;
- OA, which may be identical or different, represent an oxyethylenated, oxypropylenated or oxybutylenated radical, or mixtures thereof;
- m is equal to 0 or 1;
- n is an integer between 4 and 800.

According to one more particular embodiment of the invention, the unit (I) of the copolymer comprises a sequence of oxyethylenated, oxypropylenated or oxybutylenated radicals, or a combination of two or three of these units, the sum of the units being equal to n.

It should be noted that the copolymers forming the subject of the use according to the invention may, depending on their subsequent use, have

their structure adapted, especially via the nature and number of oxyalkylenated units. Thus, for example, the compatibility of the copolymer with a very sparingly polar compound may be increased by reducing the number of oxyethylenated radicals and/or by increasing the number of oxypropylenated or even oxybutylenated radicals.

Preferably, the number of units OA is between 4 and 300.

X corresponds to the end function of said unit after reaction with an amine or carboxylic acid function. To be more precise, X is obtained from the reaction of monomer(s) or of prepolymer(s), which are, for the copolymer forming the subject of the invention, the source of the unit (I), with an amine or carboxylic acid function.

It should be noted that it is advantageous to use prepolymers corresponding to the unit (I) which are obtained extemporaneously, and which contain end functions capable of reacting with amine or carboxylic acid functions.

Among these suitable end functions, mention may be made most particularly of alcohols, amines, carboxylic acids, epoxides and isocyanates.

Thus, when X is obtained from the reaction of an amine end function with a carboxylic acid, that is to say an amide function, X corresponds to the following function: -NH-. When X is obtained from the

reaction of an alcohol end function with a carboxylic acid, that is to say an ester function, X corresponds to the following function: -O-; and so on.

According to a first preferred embodiment of the invention, the unit (1) contains a group X resulting from the reaction of an amine function with a carboxylic acid, in which case m is 1.

According to this particular embodiment, when the radical OA is an oxyethylenated radical, the radical R^1 may contain 2 to 4 carbon atoms. When the radical OA is an oxypropylenated or oxybutylenated radical, the radical R^1 more particularly comprises 3 or 4 carbon atoms, respectively.

Such units (I) derive from polyoxyalkylenated diamines. These compounds are well known to those skilled in the art and are sold in particular under the brand name Jeffamine® (Texaco-Huntsmann).

According to a second preferred embodiment of the invention, the unit (I) contains a group X resulting from the reaction of an alcohol with a carboxylic acid, in which case m is preferably 0.

The units (I) corresponding to this variant are obtained from block or random polyalkylene glycols or polyalkylene glycol copolymers.

Compounds which may be used in the present invention are sold in particular under the brand name Pluronic PE® (BASF).

When the unit (I) contains a group X

resulting from the reaction of a epoxide or an isocyanate with an amine or a carboxylic acid, then m is preferably equal to 0.

The copolymer according to the invention may comprise only one type of unit (I) or a combination of several such units, whether these units are differentiated by the nature of their units X and/or of their units OA.

The second types of units of the copolymers used in the invention have the following formulae:

$$-[NH-R^2-NHCO-R^{2\prime}-CO]_r \qquad (IIa),$$

and/or

$$-[NH-R^3-CO]_s \qquad (IIb),$$

in which formulae:

- R^2, R'^2, R^3 and R^4, which may be identical or different, represent:
  - a linear or branched alkyl radical comprising 2 to 18 carbon atoms,
  - an aryl radical comprising one or more optionally substituted aromatic nuclei,
- r is such that the number of amide bonds is between 1 and 15 per unit (I),
- s is such that the number of amide bonds is between 1 and 15 per unit (I).

More particularly, the radicals R^2, R'^2 and R^3, which may be identical or different, represent linear or branched radicals comprising 2 to 12 carbon atoms, and preferably methylene radicals, optionally

bearing one or more methyl radicals.

According to one preferred embodiment, said radicals, which may be identical or different, are chosen in particular from divalent ethyl, 1-methylethyl, propyl, 1-methylpropyl, butyl, hexyl, heptyl, octyl, decyl, undecyl and lauryl radicals.

Another possibility consists of radicals R^2, R'^2 and R^3, which may be identical or different, representing aryl radicals comprising one or more optionally substituted aromatic nuclei.

When the abovementioned radicals comprise only one aromatic nucleus, preferably containing 6 carbon atoms, the reactive functions (carboxylic acids and/or amines) are in an ortho, meta or para position.

It should be noted that when the above-mentioned radicals comprise several aromatic nuclei, preferably two aromatic nuclei, these nuclei may be peri-fused or linked via inert groups, such as simple valency bonds or an alkyl radical comprising 1 to 4 carbon atoms.

Among the radicals comprising two aromatic nuclei, mention may be made most particularly of divalent naphthyl radicals attached to the reactive functions (carboxylic acids and/or amines) via the carbon atoms 1 and 2, 1 and 4, 1 and 5, 1 and 6, 1 and 7 or 2 and 7.

The values of r and s are more particularly between 5 and 10, per unit (I).

The units (IIa) are obtained by reacting a diamine with a diacid, and the units (IIb) are obtained by reacting amino acids or lactams.

Such units may be obtained in situ, during the preparation of the copolymer used in the invention, or alternatively may be prepared extemporaneously: these units are produced in accordance with a conventional polyamidation process, which will be described in detail hereinbelow.

Thus, according to one preferred variant of the invention, the units used as units (IIa) or (IIb) are polyamides, such as polyamide 6, polyamide 10, polyamide 11, polyamide 12 or polyamide 6,6, or a random copolymer of at least two such polyamides, in all proportions, preferably 50/50.

It should be noted that the use of units (IIa) and (IIb) which have just been described has the additional advantage of making it possible to obtain a copolymer whose melting point is not very high, thus facilitating the preparation of the gel, during which the polymer is molten.

As regards the units (III), their formula is as follows:

$$-OC-R^4-CO,$$

in which R^4, which may be identical or different, have the same meaning as that given for the radicals R^2 to R^3 mentioned above. Reference may thus be made thereto.

The units (III) are obtained from the

corresponding diacids.

The molar ratio of the number of units (III) to the sum of the number of units (I) is between 0.5/1 and 1.4/1. According to one preferred embodiment of the invention, the number of units (III) is such that it is close to the stoichiometry between the number of amine, carboxylic and optionally alcohol, isocyanate and epoxy functions.

The copolymers, or the mixture of copolymers, used in the invention also have the advantage of having a relatively low melting point, that is to say a melting point of less than about 190°C, more particularly between 70 and 190°C and preferably between 100 and 190°C.

The copolymers which have just been described may be prepared by reacting dicarboxylic acids, polyoxyalkylenated compounds containing end functions capable of reacting with amine or carboxylic acid functions (in the form of monomers or prepolymers), amino acids or lactams, or alternatively polyamides.

The process is performed by placing the various reagents in contact, preferably in the absence of solvent.

This first step is generally performed without heating. However, when one or more of the reagents is in a solid form, the operation is performed at a temperature at least equal to the highest melting point.

The various reagents are used in amounts that are suitable for obtaining a copolymer as defined above.

Once the reagents have been placed in contact, the actual polymerization reaction is performed. To do this, the temperature is raised to a value generally of between 100°C and 300°C. During this step, the reaction water is evaporated off.

The pressure conditions during the polymerization reaction may be readily determined by a person skilled in the art.

A catalyst may optionally be used to promote the polyamidation reaction, such as, for example, hypophosphorous acid, phenylphosphinic acid, phenylphosphonic acid or tris(nonylphenyl) phosphite.

A catalyst which promotes polyesterification may also be used, if necessary. Among the catalysts which may be used, mention may be made of titanium-based and zirconium-based catalysts, inter alia, such as, for example, titanium tetrabutyl orthotitanate and tetrabutyl orthozirconate.

The catalyst may represent from 0% to 1% by weight relative to the total weight of the various monomers, more particularly up to 0.5% and preferably between a few tens and a few hundreds of parts per million.

As has been mentioned previously, the copolymers used in the invention have a number-average

molar mass of less than or equal to 100 000 g/mol and more particularly between 10 000 and 50 000 g/mol.

It should be noted that the number-average molar masses of the copolymers were evaluated by steric exclusion chromatography, using polystyrene as standard.

The copolymers are more particularly used in a proportion of from 0.1% to 15% by weight relative to the relatively nonpolar compound or the surfactant. Advantageously, the copolymer content is between 0.5 and 10% by weight relative to the same reference.

In the case of a gelation of a relatively nonpolar compound, it should be noted that the copolymer used in the present invention may be combined with at least one nonionic or anionic surfactant, in order to make said relatively nonpolar compound self-emulsifying.

In such a case, the surfactant is preferably free of polar solvent or, in any case, the solvent content in this surfactant, if it is present, should be such that it does not prevent the subsequent gelation of the copolymer/surfactant/relatively nonpolar compound mixture.

Among the nonionic surfactants which are suitable, mention may be made of:

. polyoxyalkylenated (polyethoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkylphenols in which the alkyl substituent is C_6-C_{12}

and containing from 5 to 25 oxyalkylene units; examples which may be mentioned are Triton X-45, X-114, X-100 or X-102 sold by Rohm & Haas Co. and Igepal NP2 to NP17 from Rhodia Chimie;

. polyoxyalkylenated C_8-C_{22} aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units; examples which may be mentioned are the products Tergitol 15-S-9 and 24-L-6 NMW sold by Union Carbide Corp., Neodol 45-9, 23-65, 45-7 and 45-4 sold by Shell Chemical Co., Kyro EOB sold by Procter & Gamble Co., Synperonic A3 to A9 from ICI and Rhodasurf IT, DB and B from Rhodia Chimie;

. ethoxylated or ethoxy-propoxylated triglycerides of plant or animal origin, such as, for example, lard, tallow, groundnut oil, butter oil, cottonseed oil, flax oil, olive oil, palm oil, grape seed oil, fish oil, soybean oil, castor oil, rape seed oil, copra oil or coconut oil;

. products resulting from the condensation of ethylene oxide and/or propylene oxide with propylene glycol or ethylene glycol, with a weight-average molecular mass of about from 2 000 to 10 000, such as the Pluronic products (BASF);

. products resulting from the condensation of ethylene oxide and/or propylene oxide with ethylenediamine, such as the Tetronic products (BASF);

. ethoxylated and/or propoxylated C_8-C_{18} fatty acids containing from 5 to 25 ethoxylated and/or

propoxylated units;

. C_8-C_{20} fatty acid amides containing from 5 to 30 ethoxylated units;

. ethoxylated amines containing from 5 to 30 ethoxylated units;

. alkoxylated amido amines containing from 1 to 50, preferably from 1 to 25 and most particularly from 2 to 20 oxyalkylene units (preferably oxyethylene units);

. amine oxides such as (C_{10}-C_{18})alkyl dimethylamine oxides and (C_8-C_{22})alkoxyethyldihydroxyethylamine oxides;

. alkoxylated terpenic hydrocarbons such as ethoxylated and/or propoxylated α- or β-pinenes, containing from 1 to 30 oxyethylene and/or oxypropylene units; for instance those described in patent WO 96/01245;

. alkylpolyglycosides which may be obtained by condensation (for example by acid catalysis) of glucose with primary fatty alcohols (US-A-3 598 865; US 4 565 647; EP 132 043; EP 132 046, etc.) containing a C_4-C_{20} and preferably C_8-C_{18} alkyl group and also an average number of glucose units of about from 0.5 to 3 and preferably of about from 1.1 to 1.8 per mole of alkylpolyglycoside (APG); mention may be made in particular of those containing a C_8-C_{14} alkyl group and on average 1.4 glucose units per mole; a C_{12}-C_{14} alkyl group and on average 1.4 glucose units per mole; a C_8-C_{14} alkyl group and on average 1.5

glucose units per mole; a C_8-C_{10} alkyl group and on average 1.6 glucose units per mole; which are sold, respectively, under the names Glucopon 600 EC®, 600 CSUP®, 650 EC® and 225 CSUP® by Henkel.

As regards the anionic surfactants, use is made more particularly of surfactants which are in the form of liquid or in a form which is soluble in the relatively nonpolar compound. Examples which may be mentioned are:

. alkyl ester sulfonates of formula R-CH(SO_3M)-COOR′, in which R represents a C_8-C_{20} and preferably C_{10}-C_{16} alkyl radical, R′ represents a C_1-C_6 and preferably C_1-C_3 alkyl radical and M represents a cation chosen from an alkali metal or alkaline-earth metal (sodium, potassium, lithium or calcium), a substituted or unsubstituted ammonium residue (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethyl-piperidinium, etc.) or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine, etc.);

. alkyl sulfates of formula $ROSO_3M$, in which R represents a C_5-C_{24} and preferably C_{10}-C_{18} alkyl or hydroxyalkyl radical, M representing a hydrogen atom or a cation as defined above, and also the ethoxylenated (EO) and/or propoxylenated (PO) derivatives thereof, containing on average from 0.5 to 30 and preferably from 0.5 to 10 EO and/or PO units;

. alkylamide sulfates of formula $RCONHR'OSO_3M$ in which R represents a C_2-C_{22} and preferably C_6-C_{20} alkyl radical, R' represents a C_2-C_3 alkyl radical, M representing a hydrogen atom or a cation of the same definition as above, and also the ethoxylenated (EO) and/or propoxylenated (PO) derivatives thereof, containing on average from 0.5 to 60 EO and/or PO units;

. alkoxylated (ethoxylated and/or propoxylated) phosphate esters derived from aliphatic alcohols, from alkylphenols or from alkylarylphenols;

. saturated or unsaturated C_8-C_{24} and preferably C_{14}-C_{20} fatty acid salts, C_9-C_{20} alkylbenzenesulfonates, primary or secondary C_8-C_{22} alkylsulfonates, alkylglyceryl sulfonates, the sulfonated polycarboxylic acids described in GB-A-1 082 179, paraffin sulfonates, N-acyl N-alkyltaurates, alkyl phosphates, isethionates, alkylsuccinamates, alkylsulfosuccinates, sulfosuccinate monoesters or diesters, N-acyl sarcosinates, alkylglycoside sulfates and polyethoxycarboxylates;

. sophorolipids, such as those in acid or lactone form, derived from 17-hydroxyoctadecenoic acid;

. the associated cation has the same definition as that given for M, or is a hydrogen atom.

When a surfactant is present, the amount used is more particularly between 5% and 20% by weight relative to the relatively nonpolar compound.

The advantage of introducing a surfactant into the copolymer/relatively nonpolar compound mixture is that it makes the resulting gel self-emulsifying.

The copolymer according to the invention may similarly be used with a filler such as, for example, a filler of lamellar structure. By way of illustration, smectites (montmorillonite, beidellite, nontronite, hectorite, saponite, etc.) may be used.

The filler content varies within a wide range. Advantageously, and when it is present, its content may represent up to 20% by weight of the copolymer.

This filler may be used in several ways.

The first consists in using it during the preparation of the copolymer. This possibility has the surprising advantage of reducing the melting point of the copolymer thus obtained. This may prove to be advantageous when using the copolymer to prepare the gel.

The second consists in adding the filler when using the copolymer. Such an operation makes it possible to increase the hardness of the resulting gel.

Needless to say, it would not constitute a departure from the context of the present invention to combine these two variants.

One of the fields of application of the mixture comprising the copolymer and the relatively nonpolar compound or the surfactant relates to

formulations intended for cleaning or stripping paints and varnishes, on various surfaces, for example such as metals.

The advantage of this mixture according to the invention is that it makes it possible to obtain a highly viscous composition which makes the cleaning/stripping operation more efficient by means of better "attachment" of the active composition to the support to be treated.

The mixtures according to the invention may be used, for example, for cleaning/stripping vertical surfaces.

Another field of application of the mixture according to the invention relates to that of industrial detergency, for which it makes it possible to provide a means for gelling solutions comprising, for example, compounds of the type such as limonenes.

Similarly, it makes it possible to gel liquid additives for solid detergent formulations.

The mixture according to the invention may also be used in the plant protection field.

It may be advantageous to have available gelled mixtures comprising one or more active materials that are liquid, dissolved or held in suspension, in a suitable solvent, from the moment that these mixtures show solubility parameters within the ranges indicated above.

Specifically, such mixtures are stable up to

temperatures of at least about 50°C.

The mixture according to the invention may also find an application in the field of printing inks, with the gelation of mineral or plant oils, inter alia.

The mixtures according to the invention are obtained by placing the copolymer in contact with the relatively nonpolar compound or the surfactant and, where appropriate, the abovementioned additives.

This placing in contact preferably takes place with heating over a period which is sufficient to dissolve or disperse the (co)polymer. For example, a temperature of at least 90°C is suitable for carrying out the invention. Advantageously, the dissolution or dispersion may be carried out at a temperature at which the copolymer is in molten form.

In the case of the gelation of relatively nonpolar compounds, it may be that the melting point of the copolymers described previously is higher than the flash point of said relatively nonpolar compounds. Consequently, the operation of placing in contact may take place preferably under a stream of nitrogen.

The time for which the compounds are placed in contact is more particularly such that the copolymer is dissolved.

Once dissolution has been achieved, the mixture is cooled without stirring to facilitate the formation of the gel.

Concrete but nonlimiting examples of the

invention will now be given.

EXAMPLE 1

1) Preparation of the copolymer

The following reagents are placed in a glass reactor:

Compound	% by weight	Number of mols
Jeffamine ED 2003(*)	76.1	1
Adipic acid	4.9	1
Aminocaproic acid	9.5	2.19
Aminoundecanoic acid	9.5	1.43
H_3PO_2 catalyst	500 ppm	

(*) Jeffamine ED 2003 (Huntsmann); Mn = 2276 g/ml; molar ratio of ethylene oxide (EO)/propylene oxide (PO) = 37.5/5.5;

The reactor is then purged (vacuum/nitrogen) and the temperature is raised to 230°C, under nitrogen. After maintenance at this temperature for one hour, a vacuum of 1 mbar is gradually applied, over half an hour, at 230°C. These conditions are maintained for 10 minutes.

A block copolymer comprising on average 4 amide bonds per polyamide block (determined by NMR) is obtained. In addition, the number-average molar mass is about 46 400 g/mol (determined by steric exclusion chromatography; polystyrene standard).

2) Preparation of a gel

The copolymer obtained above is dissolved

while hot (above the melting of the copolymer), under a stream of nitrogen, into Rhodiasolv RPDE, sold by Rhodia Chimie (mixture of short-chain adipic acid, glutaric acid and succinic acid esters). The copolymer is present at 1% by weight relative to the Rhodiasolv RPDE.

Once the dissolution has been achieved, the mixture is cooled without stirring to facilitate the formation of the gel.

The gel is stable up to 50°C.

EXAMPLE 2

1) Preparation of the copolymer

The process is performed as in example 1, except that the composition used is as follows:

Compound	% by weight	Number of mols
Jeffamine D 2000(*)	66.6	1
Adipic acid	4.85	1
Aminocaproic acid	28.5	6.59
H_3PO_2 catalyst	500 ppm	

(*) Jeffamine D 2000 (Texaco); Mn = 2202 g/mol; polypropylene oxide.

A block copolymer comprising on average 5 amide bonds per polyamide block (determined by NMR) is obtained. In addition, the number-average molar mass is about 17 200 g/mol (determined by steric exclusion chromatography; polystyrene standard).

2) Preparation of a gel

The copolymer obtained above is dissolved

while hot, under a stream of nitrogen, into Phytorob 926-67 methyl oleate sold by Novance. The copolymer is present at 1% by weight relative to the methyl oleate.

Once the dissolution is achieved, the mixture is cooled without stirring.

The gel is stable up to 50°C.

EXAMPLE 3

1) Preparation of the copolymer with a mineral filler

The process is performed as in example 1, except that the composition used is as follows:

Compound	% by weight	Number of mols
Jeffamine D 2000(*)	66.6	1
Adipic acid	4.85	1
Aminocaproic acid	14.3	3.3
Aminoundecanoic acid	14.3	2.15
H_3PO_2 catalyst	500 ppm	
Montmorillonite (**)	X	

(*) Jeffamine D 2000 (Texaco); Mn = 2002 g/mol; polypropylene oxide

(**) Montmorillonite SCPX 1789 from Laporte, untreated.

X represents 0%, 5% or 20% by weight relative to the weight of the copolymer.

A block copolymer comprising on average 5.5 amide bonds per polyamide block (determined by NMR) is obtained.

2) Measuring the melting points

Montmorillonite content	Melting point
0%	127°C
5%	116°C
20%	111°C

EXAMPLE 4

The copolymer obtained in example 1 is dissolved while hot (above the melting point of the copolymer), under a stream of nitrogen, in PPG 400 (polypropylene glycol with a weight-average molar mass of 400 - sold by Dow). The copolymer is present at 5% by weight relative to the PPG 400.

Once the dissolution is achieved, the mixture is cooled without stirring to facilitate formation of the gel.

The gel is stable up to 50°C.

A similar result is obtained using PEG 400 (polyethylene glycol with a weight-average molar mass of 400 - sold by Dow) with 2% of copolymer.

EXAMPLE 5

The copolymer obtained in example 1 is dissolved while hot in Synperonic A7 (C_{12}-C_{14} fatty alcohol comprising 7 oxyethylenated units - sold by ICI). The copolymer is present at 2% by weight relative to the Synperonic A7.

A gel is obtained once dissolution has been

achieved, and the mixture has been cooled without stirring to facilitate formation of the gel.

EXAMPLE 6

The copolymer obtained in example 1 is dissolved while hot, in nonylphenol 10 EO (Igepal N10 - Rhodia Chimie). The copolymer is present at 5% by weight relative to the nonylphenol.

A gel is obtained once dissolution has been achieved and the mixture has been cooled without stirring to facilitate formation of the gel.

EXAMPLE 7

The copolymer obtained in example 1 is dispersed while hot in an alkylpolyglycoside comprising a C_{12}-C_{16} alkyl unit (Plantaren 1200). The copolymer is present at 5% by weight relative to the Plantaren.

A gel is obtained once the dispersion has been achieved and the mixture has cooled without stirring to facilitate formation of the gel.

EXAMPLE 8

The copolymer obtained in example 1 is dissolved while hot in a nopol containing 3 propylene oxide (PO) units and 6.5 ethylene oxide (EO) units. This product is obtained by carrying out the teaching of international application WO 96/01245.

A gel is obtained once dissolution has been achieved and the mixture has cooled without stirring to facilitate formation of the gel.